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14. ABSTRACT Direct absorption IR laser methods developed under AFOSR support have been used to study state-to-state reactive scattering dynamics under single collision conditions. Efforts over this past year have led to significant progress in several areas: i) H atom abstraction dynamics in prototypic atom+diatom (e.g. X+HD → HX(v,J)+D), atom+triatom (e.g. X+H ₂ O → HX(v,J)+ OH(v,N)) and atom+polyatom (e.g. X+CH ₃ -CH ₃) reaction systems, ii) application of novel slit discharge concentration modulation methods for ultrasensitive IR laser based detection of cold ions in supersonic jets, iii) stereodynamics of aligned collisions in rovibrationally state-selected molecules in crossed jets, iv) first efforts in extending high sensitivity IR absorption methods to reaction scattering at the gas+hydrocarbon liquid interface, which indicate surprisingly "hot", highly non-statistical product state distributions as well as direct evidence for both "direct" and "trapping/desorption" reaction channels.			
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State-to-state Thermal/hyperthermal collision dynamics of atmospheric species

3) Abstract: Status of effort

Direct absorption IR laser methods developed under AFOSR support have been used to study state-to-state reactive scattering dynamics under single collision conditions. Efforts over this past three years have led to significant progress in several areas: i) H atom abstraction dynamics in prototypic atom + diatom (e.g. $X + HD \rightarrow HX(v,J) + D$), atom + triatom (e.g. $X + H_2O \rightarrow HX(v,J) + OH(v,N)$) and atom + polyatom (e.g. $X + CH_3-CH_3$) reaction systems, ii) application of novel slit discharge concentration modulation methods for ultrasensitive IR laser based detection of cold ions and radicals, iii) collision/fragmentation dynamics of vibrationally hyperthermal molecules, iv) first efforts using confocal laser microscopy for photogeneration and probing of highly luminescent Ag nanoparticles

4) Accomplishments/New Findings

Progress in this research program over the last three years has been on multiple fronts, which are briefly summarized below

A. Quantum state-to-state inelastic scattering: "Aligning" molecules with collisions

The stereodynamics of reactive and inelastic processes is of fundamental importance in chemistry, which has stimulated keen interest in the *alignment* of rotational states via molecular collisions. The approach we have taken is based on i) supersonic cooling of IR "absorber" molecules into the lowest rotational quantum state, ii) inelastically scattering with a "collider"

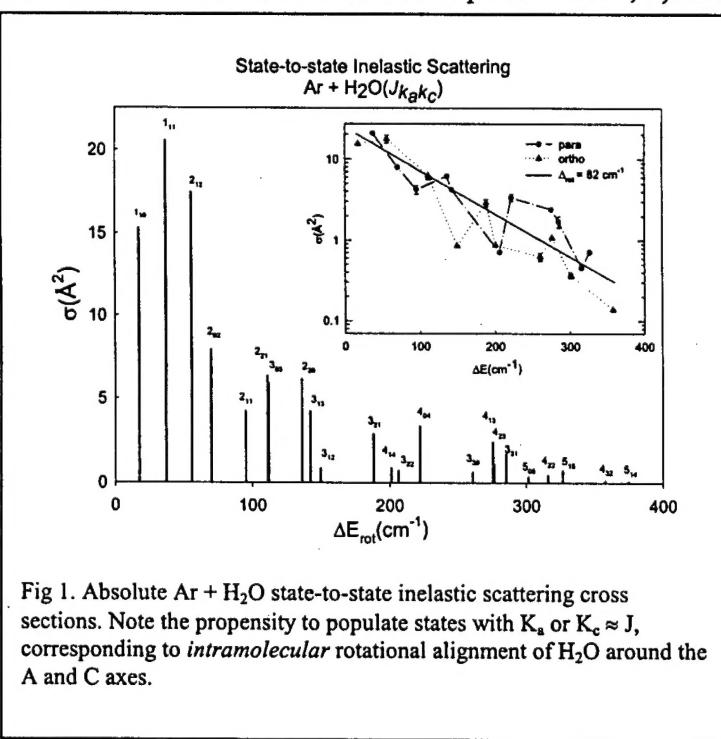
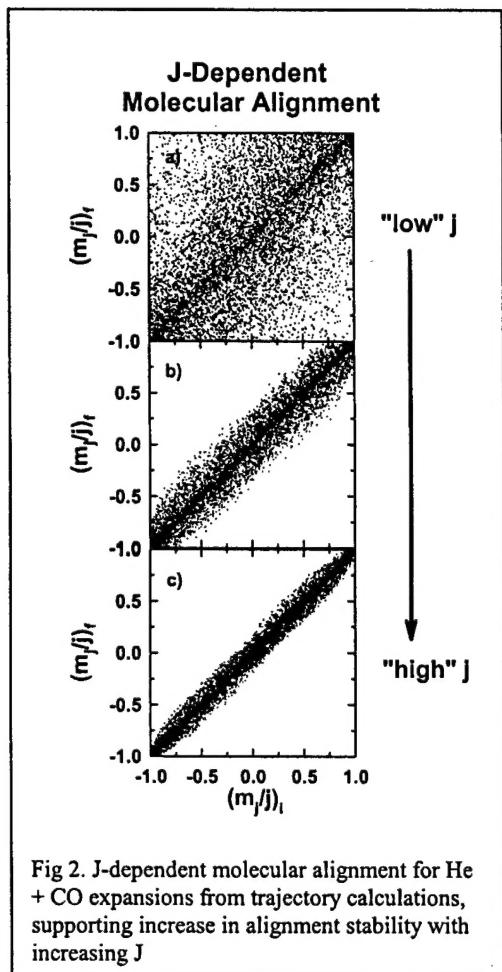


Fig 1. Absolute Ar + H₂O state-to-state inelastic scattering cross sections. Note the propensity to populate states with K_a or $K_c \approx J$, corresponding to *intramolecular* rotational alignment of H₂O around the A and C axes.

species under low density, single collision conditions, and iii) probing quantum state and Doppler velocity distributions via direct absorption with high resolution IR lasers. This novel combination of crossed molecular beams and single mode IR absorption methods provides $\geq 10^4$ fold improvement in resolution over conventional time of flight (TOF) kinetic energy loss methods, making complex molecular systems accessible for exploration at the quantum state-to-state level. Furthermore, the generality of IR absorption provides access to many closed shell atmospheric species (e.g. CH₄, H₂O, CO₂) inaccessible by other methods. Finally, absorption based methods yield *absolute* column integrated densities and *absolute* state-

to-state integral cross sections, which in conjunction with exact QM close coupling methods, permits rigorous evaluation of state-of-the-art potential surfaces.



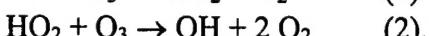
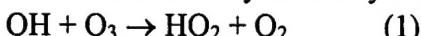
By way of example, absolute cross section data for Ar + H₂O scattering at E_{com} = 480(90) cm⁻¹ are shown in Fig. 1. The high spectral resolution readily permits differentiation between nuclear spin symmetry manifolds, and thus *simultaneous* study of collisional excitation from the lowest para (J_{KaKc} = 0₀₀) and ortho (J_{KaKc} = 1₀₁) states (see inset). Of particular dynamical interest is the significantly *nonstatistical* behavior observed for *body fixed* projections of J along the A or C axes (e.g. J_{KaKc} = 2₀₂, 2₁₁, 2₂₀ ← 0₀₀), clearly signaling *alignment* of final H₂O quantum states *in the molecular frame*. This novel *intramolecular alignment* arises from preferential solid angle access for collisional torques delivered *in-plane* (J ≈ K_c) or *around the axis* connecting the two H atoms (J ≈ K_a), as confirmed by classical trajectory calculations and full quantum calculations on semiempirical and ab initio Ar + H₂O potential energy surfaces.

Significant rotational alignment *in the lab frame* has also been observed for linear molecules in He expansions, which indicate a propensity for "pinwheel" (A₂ < 0) vs "helicopter" (A₂ > 0) motion with respect to the expansion axis, as well as increasing alignment for more rapidly rotating species. The *velocity* dependence of this alignment has been particularly controversial; direct polarization based studies on He + CO, CO₂ support an *increase* in A₂ with *increasing* speeds in the jet, while

collisional probes of He + O₂, N₂ alignment have suggested exactly the opposite trend. To help resolve these issues, we have performed extensive classical trajectory simulations of supersonic expansions on experimentally determined potentials for He-O₂, He-N₂, He-CO, and He-CO₂. These calculations unambiguously confirm that multiple rotor collisions with the faster He atoms result in a propensity for J ≈ perpendicular to the expansion axis (A₂ < 0), with alignments *increasing* dramatically for higher J due to greater "gyroscopic stability" with increasing rotation (see Fig 2). Most importantly, the calculations also indicate that molecules with J aligned *parallel* to the expansion axis (i.e. "helicopters") are indeed correlated with *faster* average velocities than molecules with j perpendicular to the axis. This validates expectations that "helicopters" present larger cross sections to accelerating collisions than "pinwheel" species, in excellent agreement with He + CO studies by Harich and Wodtke and He + N₂⁺ drift tube studies by Leone and coworkers.

B. Temperature dependent kinetic studies of OH/HO₂/O₃ chemical chain reactions

The so-called catalytic odd hydrogen (HO_x) ozone cycle,



remains one of the most important processes leading to natural destruction of atmospheric ozone, dominating the lower stratosphere (20-30 km, 190-230K) in the mid-latitude region. Indeed, the HO_x chain reaction is responsible for nearly *half* of the global ozone loss world wide, which makes accurate temperature dependent knowledge of these chain rates essential to any reliable models of atmospheric ozone phenomena. We have therefore exploited quantum state resolved direct IR laser absorption methods for an extensive temperature dependent study of OH/HO₂/O₃ chain reaction kinetics, based on time resolved IR laser direct absorption on OH(v=1←0; N). The crucial experimental advantage is that ozone is completely transparent in the near IR, permitting kinetics to be studied at much higher O₃ concentrations than previously accessible with UV/LIF methods. This is especially important as the rates slow dramatically with decreasing temperature, which has made them notoriously difficult to extract reliably under laboratory conditions. Fig 3 therefore reflect *first* rate measurements to access the 190-230 K temperature range relevant ozone chain loss in the lower stratosphere and indeed represent significantly higher than values currently used in atmospheric modeling.

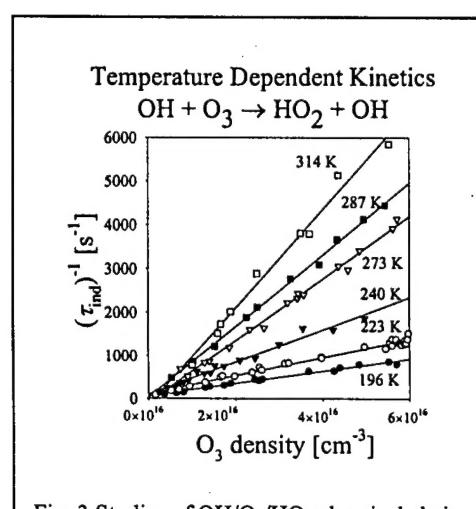


Fig. 3 Studies of OH/O₃/HO₂ chemical chain kinetics down to stratospheric temperatures

C. Energy dependent cross sections and reaction dynamics of F/F^{*} + H₂ → HF(v,J) + H

A major focus of growth during this granting period has been exploiting IR based detection methods for quantum state-to-state *reactive* scattering dynamics in crossed supersonic jets. As a

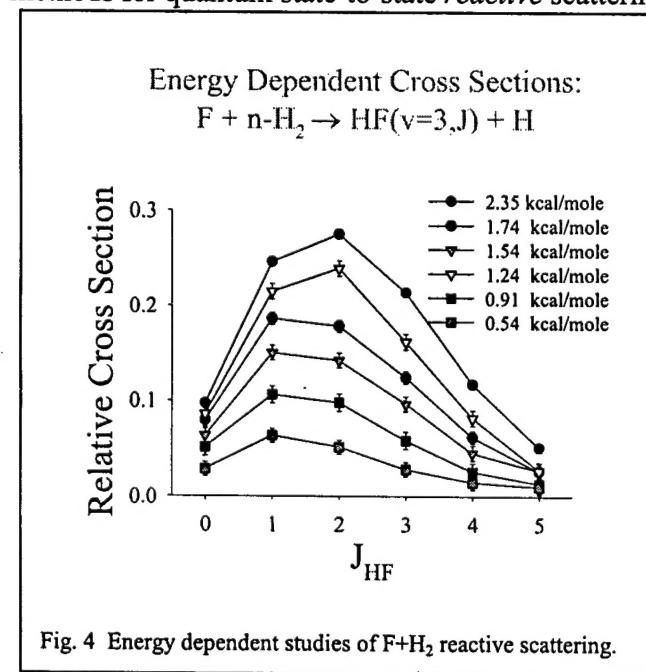


Fig. 4 Energy dependent studies of F+H₂ reactive scattering.

system of fundamental importance, we have completed a center of mass energy resolved study on reactive scattering dynamics of F + n-H₂ → HF(v,J) + H, with nascent HF(v,J) concentrations probed by near shot noise limited direct absorption methods. These high resolution IR laser methods yield fully quantum state resolved HF(v,J) distributions and integral cross sections under single collision conditions, complementing the elegant crossed beam time-of-flight energy loss studies of Neumark et al and Faubel et al as well as the optothermal HF chemical lasers studies of Keil and coworkers. What makes these IR methods experimentally feasible for reactive scattering studies are laser absorbance sensitivities at the shot noise limit (10⁻⁶/Hz^{1/2}), as well as intense

pulsed radical sources of jet cooled halogen atoms with $\geq 10^{15} \text{ #}/\text{cm}^3$ densities at the nozzle orifice.

This translates into high S/N HF absorption profiles for intersecting pulses of jet cooled n-H₂ and F with a noise floor of $\approx 10^7$ molecules/cm³/ quantum state and Doppler limited absorption signals reflecting distributions of HF(v,J) translational velocities along the probe laser axis.

As a focus of special dynamical interest, only the ground F(²P_{3/2}) spin orbit state is predicted to react *adiabatically* with H₂, despite the presence of 1.1 kcal/mole spin orbit excited F* (²P_{1/2}) at near statistical ($\approx 2:4$) concentrations in the discharge. Since the H₂ and HF bond strengths are known quite precisely (≈ 5 cm⁻¹), quantum state resolved studies at *near threshold* collision energies can be used to identify *non-adiabatic* product states that are *energetically inaccessible* on the F + H₂ surface. To address this, nascent rotational state distributions for F/F* + H₂ reactive scattering into the energetically highest HF(v=3,J) vibrational manifold have been obtained as a function of center-of-mass collision energies from E_{com} ≈ 2.4 kcal/mole down to 0.5 kcal/mole. This energy range extends substantially below the reaction barrier (≈ 1.9 kcal/mole) for the lowest *adiabatic* F(²P_{3/2}) + H₂ potential energy surface, thereby greatly magnifying the detection sensitivity to *non-adiabatic* reactions with spin orbit excited F* (²P_{1/2}) in the discharge source. Detailed analysis of the threshold data reveal *small but finite* HF(v=3,J) populations in several J states accessible only via nonadiabatic F* (²P_{1/2}) channels (even weakly visible in Fig. 4). These quantum state resolved reactive scattering studies are currently being tested against full multisurface QM calculations by Alexander, in efforts to further quantify the magnitude of non-adiabatic reaction dynamics in this fundamental chemical reaction system.

D. Quantum transition state resonance dynamics in F + HD \rightarrow HF(v,J) + D

Fascinating and remarkably diverse dynamics occur in F+HD scattering studies; simple D atom substitution leads to a “heavy + light-heavy” F--H--D transition state for F attack on the H atom, which has been predicted to support “transition state resonances” corresponding semiclassically to H atom oscillation between the F and D atoms. Indeed, there now is strong theoretical and experimental evidence for such transition state resonance dynamics at low collision energies (≈ 0.55 kcal/mol), which also predicts a characteristic “signature” in the HF(v,J) *rotational state* distributions. Specifically, transition state resonance products are thought to occur via tunneling through a strongly non-collinear barrier, which is therefore greatly enhanced by *rotational excitation* of the nascent HF in the transition state region. As a result, nascent product HF(v,J) product states at the resonance energy are predicted to yield “flat” (albeit structured J) distributions up to the energetic cutoff.

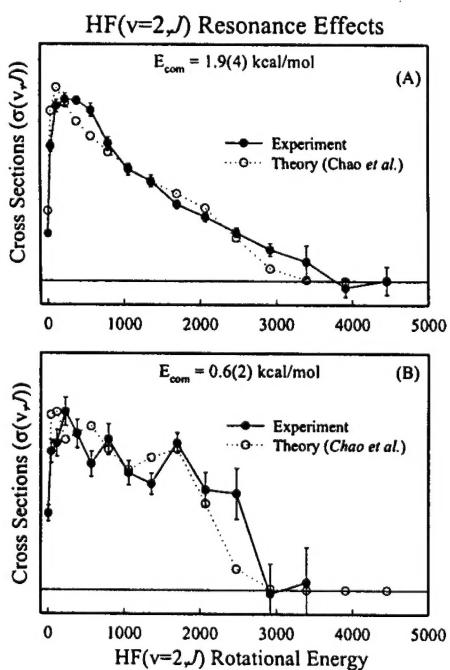


Fig 5. Nascent HF(v=2,J) product from F+HD reactive scattering at energies *above* and *at* the transition state resonance. Note the remarkable agreement with exact QM wave packet predictions.

atom, which has been predicted to support “transition state resonances” corresponding semiclassically to H atom oscillation between the F and D atoms. Indeed, there now is strong theoretical and experimental evidence for such transition state resonance dynamics at low collision energies (≈ 0.55 kcal/mol), which also predicts a characteristic “signature” in the HF(v,J) *rotational state* distributions. Specifically, transition state resonance products are thought to occur via tunneling through a strongly non-collinear barrier, which is therefore greatly enhanced by *rotational excitation* of the nascent HF in the transition state region. As a result, nascent product HF(v,J) product states at the resonance energy are predicted to yield “flat” (albeit structured J) distributions up to the energetic cutoff.

We have explored this via reactive scattering studies of F with HD, for which nuclear spin statistics also now permits jet cooling into a *single* HD(v=0, J=0) quantum state. State-resolved Doppler profiles are recorded for a series of HF rovibrational transitions and converted into state-resolved fluxes via density-to-flux analysis, yielding cross-section

data for relative formation of $\text{HF}(v,J)$ from $E_{\text{com}} \approx 1.9(4)$, down to 0.6(2) kcal/mol. State resolved $\text{HF}(v,J)$ products at all but the lowest collision energy exhibit Boltzmann-like populations, characteristic of *direct reactive scattering* dynamics. Near the transition state resonance energy ($E_{\text{com}} \approx 0.55$ kcal/mol), however, the $\text{HF}(v=2,J)$ populations exhibit a nearly “flat” distribution out to $J \approx 11$ before dropping rapidly to zero at the energetic limit, and in remarkably quantitative agreement with theoretical wavepacket predictions by Chao *et al* (see Fig. 5). These threshold studies also indicate several rotational states in the $\text{HF}(v=3)$ vibrational manifold energetically inaccessible to $\text{F}({}^2\text{P}_{3/2})$ reagent, but which are again consistent with a minor ($\approx 5\%$) *nonadiabatic* contribution from spin orbit excited $\text{F}^*({}^2\text{P}_{1/2})$ present in the discharge.

E. Quantum state-resolved atom + polyatomic scattering: $\text{F} + \text{CH}_4 \rightarrow \text{HF}(v,J) + \text{CH}_3$

In efforts to establish “benchmarks” for single collision reaction dynamics in higher dimensional systems, we have recently extended these crossed jet high resolution IR methods to atom + polyatomic reactive scattering, as in $\text{F} + \text{CH}_4 \rightarrow \text{HF}(v,J) + \text{CH}_3$. Rovibrational state-resolved HF column-integrated absorption profiles have been obtained under single collision conditions and converted to populations via detailed density-to-flux analysis. Final HF rotational states from $\text{F} + \text{CH}_4$ are observed up to the maximum energetically accessible J values in both the $v=2$ and $v=3$ vibrational manifolds, providing strong experimental support for a bent F-H-C transition state structure. Summed over all product rotational levels, the nascent *vibrational* quantum state populations for $\text{HF}(v)$ are in good agreement with previous flow cell studies by Setser, Heydtmann, and co-workers. At the *rotational* state level, however, the direct IR laser absorption methods reveal nascent distributions for $\text{HF}(v,J)$ significantly *hotter* than previously reported, presumably due to reduced collisional relaxation under supersonic jet conditions.

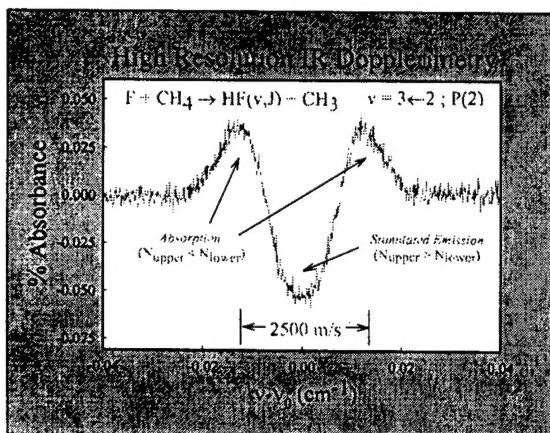


Fig. 6. High resolution Doppler profiles from $\text{F} + \text{CH}_4 \rightarrow \text{HF}(v,J) + \text{CH}_3$, with absorption/stimulated emission contributions at large and small recoil velocities, yielding information on *differential* state-resolved cross sections.

Interestingly, high-resolution IR profiles from $\text{F} + \text{CH}_4 \rightarrow \text{HF}(v,J) + \text{CH}_3$ exhibit highly structured Doppler profiles (see Fig. 6), that directly reflect nascent quantum state-resolved *translational* distributions along the probe laser direction. The novel structure results because the upper $\text{HF}(v=3)$ state has less available energy than $\text{HF}(v=2)$ to distribute into translational recoil, yielding velocity dependent population *inversion* at small Doppler detunings (i.e. *stimulated emission*) vs. a lower state population *excess* (i.e. *absorption*) at large detunings. These data have been analyzed by Monte Carlo simulations to generate lab frame Doppler profiles for a series of center of mass angular distributions, which are then fit to the experimental Doppler profiles via singular value decomposition (SVD) methods. This yields a coarse grained representation of state-resolved differential cross sections, which identify a strong propensity in $\text{HF}(v=2, \text{low } J)$ for forward/backward scattering ($|\cos(\theta)| \approx 1$) vs. side scattering ($|\cos(\theta)| \approx 0$) the center-of-mass frame.

Interestingly, high-resolution IR profiles from $\text{F} + \text{CH}_4 \rightarrow \text{HF}(v,J) + \text{CH}_3$ exhibit highly structured Doppler profiles (see Fig. 6), that directly reflect nascent quantum state-resolved *translational* distributions along the probe laser direction. The novel structure results because the upper $\text{HF}(v=3)$ state has less available energy than $\text{HF}(v=2)$ to distribute into translational recoil, yielding velocity dependent population *inversion* at small Doppler detunings (i.e. *stimulated emission*) vs. a lower state population *excess* (i.e. *absorption*) at large detunings. These data have been analyzed by Monte Carlo simulations to generate lab frame Doppler profiles for a series of center of mass angular distributions, which are then fit to the experimental Doppler profiles via singular value decomposition (SVD) methods. This yields a coarse grained representation of state-resolved differential cross sections, which identify a strong propensity in $\text{HF}(v=2, \text{low } J)$ for forward/backward scattering ($|\cos(\theta)| \approx 1$) vs. side scattering ($|\cos(\theta)| \approx 0$) the center-of-mass frame.

F. Relaxation dynamics of vibrationally hyperthermal OH

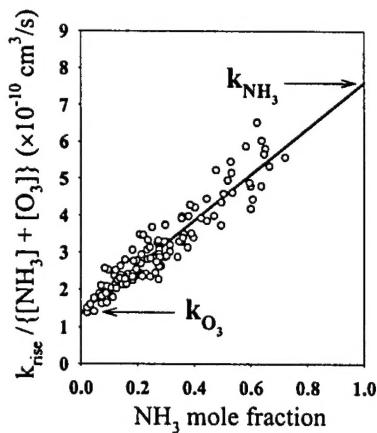


Fig. 7. Stern-Volmer plots for vibrational relaxation of OH($v=9$) by O₃ and NH₃, indicating remarkably high quenching rates for NH₃ \approx 3-4 fold faster than gas kinetic.

atoms is obtained by 193 nm photolysis of NH₃ \rightarrow NH₂ + H in a fast flow cell, followed by rapid O atom abstraction from O₃. The OH quantum state concentrations are then probed as a function of time and quantum state after the laser pulse via direct IR absorption, yielding both a single exponential rise and decay. Data for OH($v=9, N$) removal are obtained for a systematic series of O₃ and NH₃ concentrations, and analyzed via Stern-Volmer plots shown in Fig. 7. The removal OH($v=9, J$) by O₃ occurs with a gas-kinetic rate ($k_{O_3} = 1.37(15) \times 10^{-10} \text{ cm}^3/\text{s}$), which improves on

but is reasonably consistent with previous studies. Quite surprisingly, however, collisional removal of OH($v=9, N$) by NH₃ proves to be extremely fast ($k_{NH_3} = 7.60(50) \times 10^{-10} \text{ cm}^3/\text{s}$), already \approx 3-4 times higher than the hard-sphere collision limit. These differences suggest that OH($v=9$) removal by NH₃ arises from long-range, dipole-dipole V-V energy transfer with the NH₃ molecule, leading either to inelastic quenching or subsequent reaction. This study also places an conservative upper limit of $5 \times 10^{-14} \text{ cm}^3/\text{s}$ on OH($v=9$) vibrational relaxation by argon.

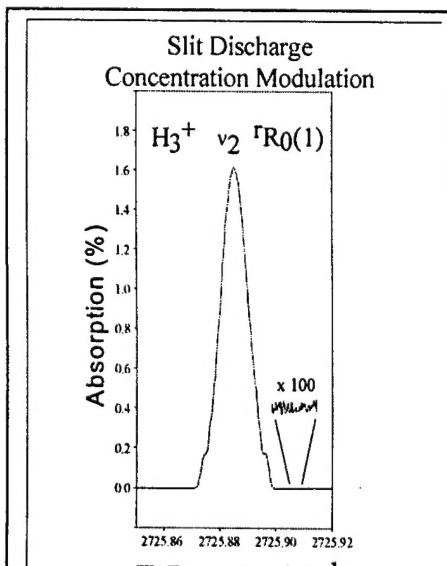


Fig. 8 High resolution scan over a single rovibrational H₃⁺ line, demonstrating enhanced detection sensitivities in 100 KHz concentration modulated discharges. Note the high S/N \approx 1000:1 feasible even for molecular ions

G. Concentration modulated sources of hyperthermal jet cooled ions and radicals

The crossed jet reactive scattering studies rely on high concentrations of transient radical species, in a discharge be tightly confined in a 1 mm region *behind* the expansion orifice. This permits discharge operation at high ($\approx 1-10 \text{ A/cm}^2$) current densities with efficient rotational cooling ($T_{rot} \approx 10-20 \text{ K}$) in the post discharge expansion, and thereby delivering $> 10^{11}-10^{12} \text{ cm}^{-3}$ densities of jet cooled radicals to the laser probe region.

Recently, we have significantly extended this capability by implementing fast (≈ 100 KHz) current modulated discharges with pulsed slit supersonic expansions. The high modulation frequency permits ≈ 100 current cycles per 1 msec expansion pulse, which permits phase sensitive detection of absorbance signals from radicals (or other transient species) scattering, either reactively or inelastically, from the collision region. In conjunction with high frequency lockin detection via double balanced mixers, these new sources have resulted in shot noise limited detection sensitivities down to 7.3×10^{-7} absorbance/Hz $^{1/2}$. Sample direct absorption data for H₃⁺ molecular ion are shown in Fig 8 revealing S/N $\approx 1000:1$. In particular, this capability for fast radical pulses will prove invaluable in the proposed studies of reactive/inelastic scattering from liquid surfaces, as well as in studies of translationally hyperthermal collision dynamics.

H. Photofragmentation/reaction dynamics in vibrationally hyperthermal systems

We have also initiated steps in the crossed jet apparatus to explore state-to-state reaction dynamics of vibrationally hyperthermal reagents. Target chromophores (such as H₂O) are supersonically expanded and cooled into lowest rotational states allowed by nuclear spin statistics, and pumped into a single rovibrational state by IR excitation from a narrow band pulsed optical parametric oscillator (OPO) in overtone ($\Delta v=2, 3$) regions. These vibrationally hyperthermal molecules will be crossed by a jet cooled radicals (F, Cl) from the pulsed discharge source. The IR laser pre-excitation facilitate H atom abstraction selectively in the vibrationally labeled species, the final quantum state products of which can be probed by sensitive LIF and/or REMPI detection. These studies will therefore build on the elegant vibrationally mediated reaction experiments,¹⁵¹⁻¹⁵⁶ but with powerful additional advantages of i) jet cooled reagents, ii) single collision conditions and iii) a well defined *alignment* of the relative velocity vector with respect to the laboratory frame.

Significant progress in this direction has already been demonstrated via simple photolysis of quantum state-selected H₂O in supersonic jets (Fig. 9), in effect exploiting a ≈ 1 mJ photolysis laser pulse as preliminary substitute for the Cl radical beam. Specifically, jet expansions of supersonically cooled ortho (J_{KaKc} = 1₀) H₂O in Ar have been pumped by IR OPO excitation into specific J_{KaKc} = 0₀₀ or 2₀₂ levels of the |02> vibrational overtone manifold, selectively dissociated into H + OH(² Π) by 193 nm photolysis, with final OH product states probed by LIF on the A-X band. The high S/N ≈ 2000 attests to the sensitivity of the LIF method, but *overpredicts* the crossed beam experimental S/N by the ≈ 40 fold higher “absorbance probability” (i.e. fluence x cross section) for photon vs. radical sources. When these relative absorbance probabilities are correctly taken into account, the predicted S/N is $\approx 50:1$, which is consistent

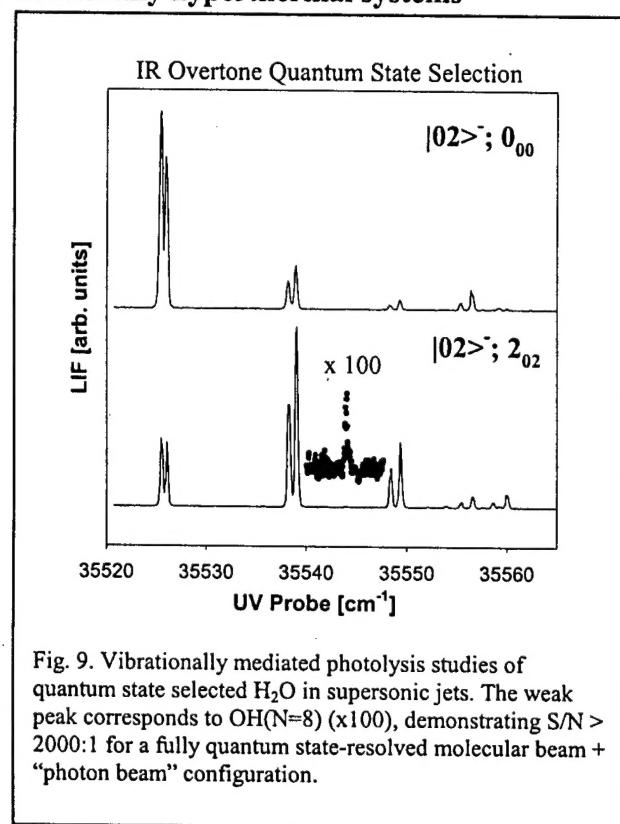


Fig. 9. Vibrationally mediated photolysis studies of quantum state selected H₂O in supersonic jets. The weak peak corresponds to OH(N=8) (x100), demonstrating S/N $> 2000:1$ for a fully quantum state-resolved molecular beam + “photon beam” configuration.

with the estimates described above and clearly underscores the feasibility of such vibrationally mediated studies under crossed beam conditions.

I. Confocal Microscopy of Luminescent Silver Nanoparticles

We are also initiating new efforts into single molecule microscopy of silver nanostructures. Silver particles are capable of sustaining resonant collective electron oscillations,

the so-called surface plasmons; interestingly these surface plasmon modes may be optically excited in the near-ultraviolet or visible range of the electromagnetic spectrum. The collective electron motion in a surface plasmon leads to exceptionally strong local electric fields, giving rise to a number of interesting phenomena, in particular surface-enhanced Raman spectroscopy (SERS) of surface-adsorbed molecules. Quantitative elucidation of the enhancement mechanism and extension of ensemble-averaged SERS to the single molecule limit is of keen interest to ultrasensitive detection methods. In our preliminary work, we have developed novel methods for visible light-induced photogeneration of silver nanoparticles in thin polymer films. Specifically, the method produces strongly luminescent *diffraction-limited* clusters of stable silver nanoparticles using a conventional confocal microscope set-up. The strong luminescence can be attributed to a surface-enhanced

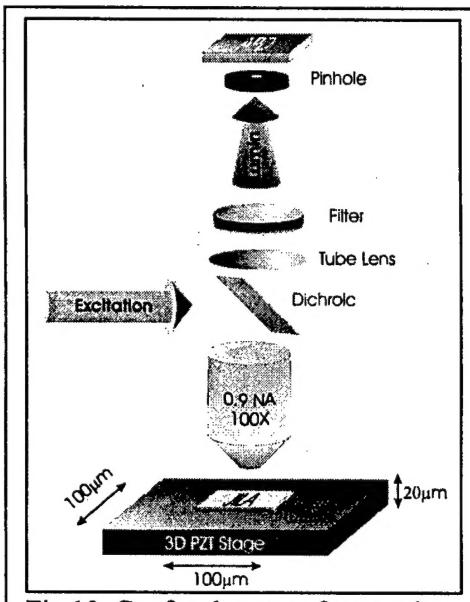


Fig 10. Confocal system for creating luminescent Ag nanoparticles

Raman scattering process from molecules on the surface of the silver particles.

The optical set-up consists of a conventional upright microscope equipped with a dry objective (100x, 0.90 NA) (see Fig 10). Excitation is provided by either an argon-ion laser (air-cooled, 488 nm, 5 mW), a Nd:YVO₄ laser (532 nm, 5 mW) or a green Helium-Neon (HeNe) laser (543.5 nm, 4 mW), coupled into a single-mode optical fibre for spatial filtering. The excitation beam is reflected off a dichroic beam splitter, designed to reflect excitation light and transmit red-shifted luminescence, and brought to a nearly diffraction-limited spot (full-width half maximum $\Gamma_{FWHM} \approx 350$ nm). This focused cw light source in silver perchlorate/polystyrene thin films generates well defined Ag nanostructures, which undergo strong optical luminescence, collected by the same objective in the epifluorescence geometry. Residual excitation light is suppressed using a combination of two interference filters (optical density > 6) and the luminescence is focused onto the aperture of a multimode fibre (100 μm core diameter) acting as a confocal pinhole. In the imaging mode, the fibre is directly coupled to a single-photon counting avalanche photodiode with approximately 90 counts per second (cps) dark counts.

Sample "read-write" images recorded after photogenerating Ag nanostructures in the AgClO₄/polystyrene film are shown in Fig. 11, which shows a 20 μm x 20 μm region with a regular array of photogenerated, diffraction-limited luminescent features. Each individual feature

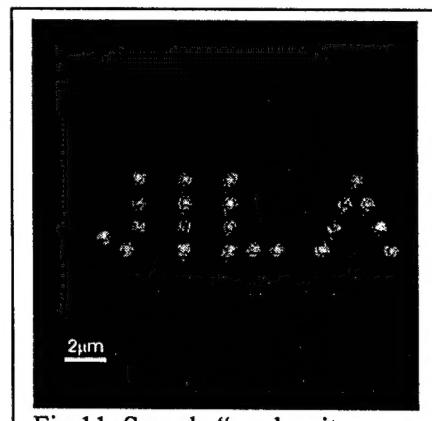


Fig 11. Sample "read-write" images in Ag nanoparticles

is generated by illuminating for several seconds at an intensity of 50 kW/cm² at 488 nm. After writing the desired pattern, an image was acquired at 488 nm with a low excitation intensity of 0.5 kW/cm² and a dwell time per pixel of 1 ms. The features are spatially confined to the area of the laser focal spot when writing and display a very high contrast ratio of approximately 200:1. Similar images have been recorded at multiple laser wavelengths (488 nm, 532 nm, and 543 nm). Intense illumination of silver perchlorate embedded in a polymer matrix thus leads to *localized* generation of a luminescent species.

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- 1) Sergey Nizkorodov (postdoc)
- 2) Warren Harper (postdoc)
- 3) Erin Whitney (graduate student)
- 4) Alex Zolot (graduate student)
- 5) Mike Wojcik (postdoc)
- 6) Mike Ziemkiewicz (graduate student)

6) Publications resulting from AFOSR supported projects (1999-present)

- 1) W. B. Chapman, A. Kulcke, B. W. Blackmon and D. J. Nesbitt, "Rotationally inelastic scattering of jet cooled H₂O with Ar: State-to-state cross sections and rotational alignment effects", *J. Chem. Phys.* 110, 8543 (1999).
- 2) S. A. Nizkorodov, W. W. Harper and D. J. Nesbitt, "State-to-state reaction dynamics in crossed supersonic jets: threshold evidence for non-adiabatic channels in F + H₂", *Faraday Disc.* 113, 107 (1999).
- 3) J. R. Fair and D. J. Nesbitt, "Dynamics of Collisional Alignment in Supersonic Expansions: Trajectory Studies of He + CO, O₂ and CO₂", *J. Chem. Phys.* 111, 6821 (1999).
- 4) S. A. Nizkorodov, W. W. Harper, W. B. Chapman, B. W. Blackmon and D. J. Nesbitt, "Energy dependent cross sections and non-adiabatic reaction dynamics in F(²P_{3/2}, ²P_{1/2}) + n-H₂ → HF(v,J) + H", *J. Chem. Phys.* 111, 8404 (1999).
- 5) S. A. Nizkorodov, W. W. Harper, B. W. Blackmon and D. J. Nesbitt, "Temperature dependent kinetic studies of the OH/HO₂/O₃ chain reaction by time resolved high resolution laser absorption spectroscopy", *J. Phys. Chem.* 104, 3964 (2000).
- 6) W. W. Harper, S. A. Nizkorodov, and D. J. Nesbitt, "Quantum state-resolved reactive scattering of F + CH₄ → HF(v,J) + CH₃: Nascent HF(v,J) product state distributions", *J. Chem. Phys.* 113, 3670 (2000).
- 7) W. W. Harper, S. Nizkorodov and D. J. Nesbitt, "Differential scattering dynamics of F + CH₄ → HF(v,J) + CH₃ via high resolution IR laser Dopplerimetry", *Chem. Phys. Lett.* 335, 381 (2001).

- 8) S. A. Nizkorodov, W. W. Harper and D. J. Nesbitt, "Fast vibrational relaxation of OH(v=9) by ammonia and ozone", *Chem. Phys. Lett.* 341, 107 (2001).
- 9) S. Davis, M. Farnik, D. Uy and D. J. Nesbitt, "Concentration modulation spectroscopy with a pulsed slit supersonic discharge expansion source", *Chem. Phys. Lett.* 344, 23 (2001).
- 10) W. W. Harper, S. A. Nizkorodov and D. J. Nesbitt, "Reactive scattering of F + HD → HF(v,J) + D: HF(v,J) nascent product state distributions and evidence for quantum transition state resonances", *J. Chem. Phys.* 116, 5622-5632 (2002).
- 11) M. Farnik, S. Davis, M. A. Kostin, O. L. Polyansky, J. Tennyson and D. J. Nesbitt, "Beyond the Born-Oppenheimer approximation: High resolution overtone spectroscopy of H₂D⁺ and D₂H⁺", *J. Chem. Phys.* 116, 6146-6158 (2002).
- 12) V. V. Protasenko, M. K Kuno, A. Gallagher and D. J. Nesbitt, "Fluorescence of single ZnS overcoated CdSe quantum dots studied by apertureless near-field scanning optical microscopy", *Optics Communications* (in press).
- 13) M. K. Kuno, D. P. Fromm, S. T. Johnson, A. Gallagher and D. J. Nesbitt, "Modelling Distributed Kinetics in Isolated Semiconductor Quantum Dots", *Phys. Rev. B* (submitted).
- 12) S. A. Nizkorodov, M. Ziemkiewicz, T. L. Myers and D. J. Nesbitt, "Vibrationally mediated dissociation dynamics of H₂O in the v_{OH} = 2 polyad", *J. Chem. Phys.* (submitted).
- 13) O. L. A. Monti and D. J. Nesbitt, "Visible Light-Induced Generation of Silver Nanoparticles", *J. Phys. Chem.* (submitted).

7) Interactions/Transitions

Invited Talks (1999-present) acknowledging AFOSR support

"Watching molecules touch: From high resolution spectroscopy of clusters to atomic force microscopy", Departments of Physics and Chemistry, Wesleyan University, Middletown, CT, January 29, 1999.

"State-to-state reaction dynamics in crossed supersonic jets", Department of Physics, University of Connecticut, Storrs, CT, January 30, 1999.

"Clusters, radicals and nanoparticles: From state-to-state reactions dynamics to near field microscopy", Department of Chemistry, U. C. San Diego, La Jolla, CA, February 23, 1999.

"High resolution full and half collision studies of intermolecular potentials", UK Collaborative Computational Project on Heavy Particle Dynamics (CCP6), University of Aberdeen, Aberdeen, Scotland, April 13, 1999.

"Chemical physics with lasers: From state-to-state collision dynamics to single molecule spectroscopy", Department of Physics and Astronomy, University of Delaware, Newark, DE, April 21, 1999.

"Collisional Dynamics of Rotational Alignment", Molecular Aspects of Gas Dynamics, National Academy, Perugia, Italy, June 19, 1999.

"Experimental/theoretical studies of state-to-state collision phenomena: Rotational alignment and non-adiabatic reaction dynamics", Conference on Molecular Energy Transfer XVI, Assisi, Italy, June 22, 1999.

"State-to-state reaction dynamics in crossed supersonic jets: threshold evidence for non-adiabatic channels in F + H₂", Faraday Disc., Leeds, UK, July 6, 1999.

"From radical spectroscopy to near field microscopy", Department of Chemistry, University of Birmingham, Birmingham, UK, July 8, 1999.

"Chemical physics with lasers: From state-to-state collision dynamics to single molecule microscopy", Department of Chemistry, Oxford University, July 12, 1999.

"State-to-state reactive scattering in crossed supersonic jets", Department of Chemistry, University College London, London, UK, July 14, 1999.

"Non-adiabatic reaction dynamics in F + n-H₂ from IR laser based state-to-state reactive scattering studies", American Chemical Society (218th National Meeting), New Orleans, LA, August 23, 1999.

"Single particle microscopy above and below the diffraction limit", Optical Society of America, Santa Clara, CA, September 28, 1999.

"Chemical physics with lasers: From slit jet discharges to single molecule spectroscopy", Department of Chemistry, University of Wisconsin, Madison, WI, October 26, 1999.

"Where Chemistry meets Physics", CU Wizards Science Outreach Program, Department of Chemistry, University Colorado, Boulder, CO, October 30, 1999.

"From state-to-state reaction dynamics to single molecule microscopy", Department of Chemistry, University of Maryland, College Park, MD, November 11, 1999.

"Chemical dynamics with a twist: From state-resolved reactions in supersonic jets to single molecule microscopy", Department of Chemistry, University of Southern California, Los Angeles, CA, January 10, 2000.

"Chemical kinetics with a twist: From state-to-state reaction dynamics to single molecule microscopy", Department of Chemistry, University of Arizona, Tucson, AZ, January 24, 2000.

“Microscopy at and below the diffraction limit via resonant scattering and laser induced fluorescence: Recent progress from apertureless NSOM”, American Physical Society, Minneapolis, MN, March 21, 2000.

“Probing quantum state to state dynamics: From clusters to chemical reactions”, American Chemical Society (219th national Meeting), San Francisco, CA, March 26, 2000.

“From Single Collisions to Single Molecules”, Institute for Physical Chemistry, University of Goettingen, Goettingen, Germany, April 13, 2000

“Spectroscopy above and below the diffraction limit”, Max Planck Institute for Biophysical Chemistry, Goettingen, Germany, April 28, 2000.

“State-resolved IR Laser Studies of Fundamental Reaction Dynamics”, Atomic and Molecular Interactions Gordon Conference, New London, NH, July 4, 2000.

“Spectroscopy, kinetics and single collision dynamics via high resolution IR laser studies of radicals”, 16th International Symposium on Gas Kinetics, Cambridge, UK, July 23, 2000.

“Dynamics: From Single Collisions to Single Molecules”, King Lecture, Department of Chemistry, Kansas State University, Manhattan, KA, September 28, 2000.

“Laser/FTIR Slit Jet Studies of Hydrogen Bonded Clusters”, Optical Society of America – Interdisciplinary Laser Science National Meeting, Providence, RI, October 23, 2000.

“Chemical Physics at the Single Molecule Level: From Quantum Dots to Biomolecules”, National Institute for Standards and Technology, Gaithersburg, MD, November 17, 2000.

“Dynamics from Single Collisions to Single Molecules”, California Institute of Technology, Pasadena, CA, Jan 16, 2001.

“From Single Collisions to Single Molecules”, Stanford University, Palo Alto, CA, February 12, 2001.

“Chemical Physics: One Molecule at a Time”, JILA Colloquium Series, University of Colorado, Boulder, CO, April 10, 2001.

“High Resolution IR Studies of Hydrogen Bonded Clusters: Large Amplitude Dynamics in (HCl)_n”, Faraday Discussion, University of Durham, Durham, UK, April 19, 2001.

“Photoluminescence Kinetics and Dynamics in Semiconductor Nanocrystals”, CLEO/QELS 2001, Baltimore, MD, May 6, 2001.

“IR Laser Studies of Radicals: From Spectroscopy to Dynamics”, 26th Int'l Symposium on Free Radicals, Assisi, Italy, September 7, 2001

“Chemistry of Cooking”, CU Wizard Science Outreach Program, University of Colorado, Boulder, CO September 29, 2001

“Radicals, Reactions and Really Small Samples”, Department of Chemistry, University of North Carolina, Chapel Hill, NC, October 4, 2001

“Quantum State-resolved Dynamics: Radicals, Reactions and Really Small Samples”, Department of Chemistry, Tufts University, Somerville, MA, November 6, 2001

“From Single Collisions to Single Molecules”, Department of Chemistry, University of Illinois, Champaign-Urbana, IL, January 23, 2002

“From Single Collisions to Single Molecules”, Department of Chemistry, University of Helsinki, Helsinki, Finland, February 1, 2002

“Reaction Dynamics at the Quantum State-to-State Level”, Department of Chemistry, University of Gothenburg, Gothenburg, Sweden, February 4, 2002

“Radicals, Reactions and Really Small Samples”, Department of Chemistry, University of Aarhus, Aarhus, Denmark, February 6, 2002

“High Resolution IR Laser Studies of State-to-state Dynamics”, American Chemical Society (223rd National Meeting), Orlando, FL, April 11, 2002.

“Searching for Simplicity: Single Frequencies, Single Collisions and Single Molecules”, Bourke Medal Lecture, Oxford University, Oxford, England, April 22, 2002.

“Searching for Simplicity: Single Frequencies, Single Collisions and Single Molecules”, Bourke Medal Lecture, University of Sussex, Sussex, England, April 24, 2002.

“Searching for Simplicity: Single Frequencies, Single Collisions and Single Molecules”, Bourke Medal Lecture, University of Durham, Durham, England, April 26, 2002.

“Searching for Simplicity: Single Frequencies, Single Collisions and Single Molecules”, Bourke Medal Lecture, University of Birmingham, Birmingham, England, April 29, 2002.

Consulting/Advisory Functions:

Advisory interactions with colleagues at Air Force Research Laboratory (Dr. James Dodd, Dr. Steve Lipson) regarding their radical kinetics program relevant to “airglow” in the upper atmosphere. Contact with Hanscomb AFB; hosted James Dodd in Boulder to present a talk on kinetics studies.

Advisory committee, Molecular Spectroscopy Symposium (1995-present), Advisory committee, International Meeting on Near Field Optics (2000-present), Organizer for the OSA-ILS symposium

on single molecule detection/near field imaging, Organizer for the ACS national meeting symposium on Molecular Alignment

ACS Program Vice-Chair Elect for Physical Chemistry (2001-02)
ACS Program Vice-Chair for Physical Chemistry (2002-03)
ACS Program Committee for Physical Chemistry Division (2000-05)
Journal of Chemical Physics, editorial board (2001-present)
Journal of Physical Chemistry, editorial board (2002-present)

8) Inventions and Patent disclosures:

None

9) Honors, Awards or Fellowships received (1999-2002)

American Physical Society Fellow
William F. Meggers Award, Optical Society of America, 1999
King Lecture, Department of Chemistry, Kansas State University, Fall 2000
Alexander von Humboldt Fellowship, Humboldt Foundation (2000-present)
Visiting Professor, Institute for Physical Chemistry, University of Goettingen,
Goettingen, Germany, Spring 2000
Visiting Professor, Max Planck Institute for Biophysical Chemistry, Nikolausberg,
Germany, Spring 2000
Bourke Medal Lectureship, Royal Society of Chemistry, Faraday Division, UK (2002).
Visiting Professor, University of Stuttgart, Spring 2002
Visiting Professor, University of Heidelberg, Spring 2003